Investigation of Coastal CDOM Distributions Using In-Situ and Remote Sensing Observations and a Predictive CDOM Fate and Transport Model

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LONG-TERM GOALS

Our long-term goal is to interpret chromophoric dissolved organic matter (CDOM) sources, distributions, and dynamics in and around the NY/NJ Harbor Estuary, with a focus on significant freshwater events, through the creation of a robust, deterministic, high-resolution, four-dimensional, predictive model of CDOM fate and transport, validated against in-situ and remote sensing observations.

OBJECTIVES

An existing four-dimensional hydrodynamic and CDOM source tracking model will be updated and and compared against a) concurrent datasets of in situ (EcoShuttle) CDOM observations available for the New York/New Jersey Harbor and, b) satellite-derived (SeaWiFS) surface CDOM distributions for the Harbor and its New York Bight Approaches (Bight Apex). The New York Harbor Observation and Prediction System (NYHOPS), a hydrodynamic/CDOM forecasting model incorporating CDOM fluorescence source strengths and first-order decay through photodegradation, will be updated to a new high-horizontal-resolution version shown to better capture the relevant hydrodynamic scales and associated CDOM sources and transport. The NYHOPS CDOM fate module will also include a more robust and deterministic bio-kinetic formulation of CDOM absorption loss due to photobleaching. Existing high-resolution local observations of CDOM fluorescence, absorption and other related variables, will be used to locally calibrate not only the NYHOPS bio-kinetic modules, but also a new CDOM remote sensing retrieval algorithm based on SeaWiFS satellite multi-channel data and a novel, coupled atmospheric-oceanic, radiative transfer and bio-optical algorithm developed at Stevens. CDOM distributions based on NYHOPS will be compared to both the in-situ observations and the SeaWiFS-derived spatial distributions, which will include chlorophyll, to continue interpretation of the CDOM data and facilitate an understanding of the processes that control CDOM distributions in estuarine and coastal waters.

The goal of this project is to interpret CDOM distributions in the New York/New Jersey Harbor and New York Bight system by comparing complementary information from the NYHOPS/CDOM fate and transport model, *in situ* data, and satellite-derived imagery. The objective here is to put the CDOM distributions and sources in perspective, through comparison of multiple data sources, as well as to other water-clarity-related agents such as chlorophyll and turbidity. In particular, we will focus on

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Form Approved OMB No. 0704-0188 significant freshwater events, testing the hypothesis that CDOM originating within the NY/NJ Harbor estuary can dynamically influence the CDOM distributions in the NY Bight.

APPROACH

The acronym CDOM stands for the chromophoric (colored) fraction of dissolved organic matter. It is used to define a generic pool of chromophoric polymers made out of carbon, nitrogen, phosphorus, silica, sulfur, etc. It is oftentimes associated with humic (high-molecular weight) and especially fulvic (yellow $C_{135}H_{182}O_{95}N_5S_2$) acids left from decaying organic matter through microbial metabolism. Although most of it is believed to be soluble in water at any pH, a small fraction may also be colloidal (Wells 2004). In this proposal the small colloidal portion of CDOM is ignored and all of CDOM is assumed to be, true to its name, in dissolved form.

CDOM attenuates light through absorption and emits it as fluorescence. Its absorption spectrum resides mostly in the ultraviolet, but has a long and very important tail at the visible wavelengths, mostly in the purple-blue range, critical for underwater visibility, mine detection, narrow-band optical communication, and other Navy matters, as well as water quality considerations such as light-limited algal growth and seagrass and coral bed sustainability. Many studies have shown that CDOM may be responsible for up to 90% or more of the total light absorption coefficient at 440 nm in coastal waters and river plumes [e.g., Ferrari and Dowell 1998, Odriozola et al 2007]. That absorption spectrum, seen as a spectrum of absorption coefficients at different wavelengths, is thought to be CDOM's contribution to the water's Inherent Optical Property (IOP) of absorption, dependent only on the contents of the water, and regardless of incoming light and its radiative transfer through the water column. Other contributors to the absorption IOP are, the water itself, phytoplankton (chl-a), and nonalgal-particulates. The latter non-algal-particulate pool, usually correlated with total suspended solids or turbidity, defines a second IOP, scattering. Based on these two IOPs, mechanistic (e.g., Kirk 1981 1984 1989) or simplified (e.g., Gallegos 2001, Biber et al 2008) radiative transfer models may be used to estimate and/or predict the water's diffuse attenuation coefficient K_d , an ambient-light-fielddependent Apparent Optical Property (AOP) of water, correlated to measures of water clarity like the Secchi depth.

Miller (2006) estimated that surface-water CDOM IOPs depend greatly on the seasons in most offshore oceanic regions, the major exception being at the Horse Latitude regions (around 30-35° N and S), where approximately 60% of the CDOM variance cannot be attributed to seasonal variation or long-term trends. In locations closer to the coast, CDOM-related IOPs may be highly variable. In fact, the water's CDOM-related absorption spectrum may change as a) CDOM spectral absorption coefficients decrease as the chromophores of newly formed CDOM undergo photolysis though exposure to sunlight in a process called photobleaching or CDOM fading (Miller 2005), b) faded CDOM mixes with younger CDOM originating either from terrestrial sources (Chen *et al* 2004 2006, Zepp 2004) or from decaying local algal detritus (McKnight *et al* 2000), and c) water-borne CDOM is lost, either through sorption to settling particles in sedimentary depositional environments, or through bacterial decomposition of faded CDOM broken down to more biologically-labile lower-molecular-weight compounds (Moran and Zepp 1997). Thus, in coastal waters close to terrestrial CDOM sources, CDOM-associated light absorption and attenuation are inherently Lagrangian processes, related to time-and-place-specific physicochemical phenomena, including terrestrial source strengths, tidal and estuarine circulation hydrodynamics, photochemical kinetics, and possibly-present local

sources (e.g., algal detritus in shallow environments with significant submerged aquatic vegetation) and sinks (e.g., sorption in depositional environments).

In 2005, ONR sponsored a dual two year effort involving both observations and dynamic modeling to investigate CDOM distributions and dynamics in New York Harbor and vicinity. In support of this effort and a related NSF-funded one, a multitude of *in situ* data were collected outside the Harbor in the New York Bight (LATTE experiment, springs of 2004-2007, http://marine.rutgers.edu/cool/latte), as well as in tributaries and embayments inside the Harbor (Chen *et al* 2005 2006). The collections inside the harbor were used to identify CDOM source strengths, while the ones outside the harbor were used to follow the transformations of CDOM as it is transported down the New Jersey Shelf and diluted with resident sea water. With regard to the Hudson tributaries, CDOM endmember concentrations were found to photodegrade or biodegrade by 30% in incubation experiments (Chen *et al* 2006).

At the same time, an ONR-funded dynamic modeling effort was underway at Stevens Institute of Technology (Stevens), supported by the abovementioned observations (Blumberg 2007). The objective there was to develop a capability for incorporating CDOM source strengths and chemical processes into the operational 4-dimensional hydrodynamic New York Harbor Observation and Prediction System (NYHOPS). The first year objective (2006) was to build CDOM into NYHOPS and conduct simulations of CDOM distributions initially treating CDOM as a conservative tracer. In the second year (2007) NYHOPS and its CDOM component were updated to a higher-resolution model grid (Fig. 1), CDOM sources and strengths in the model were updated based on comparisons of the preliminary model and field observations (Fig. 2 and Fig. 3), and photodegradation of CDOM at the water surface due to incoming sunlight was included based on a 0.168/day first-order decay rate measured in the laboratory incubation experiments. The CDOM fluorescence source strengths identified ranged from 40 QSU for the Hudson River, to 200 QSU for the Port Richmond treatment plant (Fig. 3). For comparison, fluorescence of CDOM in the Mississippi River over several years is estimated to be on the order of 50 QSU (Conmy et al 2004). The NYHOPS model CDOM fluorescence predictions helped explain CDOM distributions observed in Hackensack River in October 2006 and April 2007 (Blumberg 2007). The updated NYHOPS/CDOM high-resolution forecasting model has been made available on a daily basis to ONR and the general public over the world-wide-web since March 30th 2007 (example output in Fig. 4 and www.stevens.edu/maritimeforecast).

Satellite data can also be used to infer marine constituents in coastal waters. Chang and Gould (2006) compared CDOM spectral absorption inferred from SeaWiFS and MODIS satellite imagery through standard post-processing algorithms versus mooring data observed at the Long-Term Ecological Observatory site (LEO-15) in the New York Bight, New Jersey shelf, collected during the ONR-sponsored 2001 Hyperspectral Coastal Ocean Dynamics Experiment (HyCODE program). They found that the surface mooring-based total absorption coefficient at 440 nm, $a_{pg}(440)$, ranged from 0.4/m to 1.0/m between June 19, and Aug 08, 2001, partly due to fluctuations in chl-a (primarily) and CDOM (secondarily) and detrital concentrations. CDOM and detrital absorption dominated total absorption in bottom waters. For comparisons between satellite-derived and mooring measurements of $a_{pg}(412)$ they found mean relative errors of -69.4% (-67.1%), -52.6% (-48.9%), and -62.7%(-65.4%) for the SeaDAS-standard Arnone, GSM, and QAA algorithms for SeaWiFS (MODIS), respectively.

Recently, researchers at Stevens developed and implemented a novel algorithm of coupled atmospheric and oceanic (CAO) radiative transfer model based on the linearized discrete ordinate method (LDISORT) and a bio-optical model, to retrieve two aerosol and three marine constituents from

SeaWiFS data obtained over the Santa Barbara Channel, CA, in February 2003 (Li *et al* –accepted; Fig. 5). The three marine parameters retrieved are chlorophyll concentration, combined absorption of detritus and CDOM at 443nm, and backscattering coefficient at 443 nm. The retrievals rely on the use of an accurate forward radiative transfer model (CAO-LDISORT, Spurr *et al* 2007) in conjunction with an optimal estimation (OE) inversion scheme that relies on a bio-optical model of absorption and scattering (Zhang *et al* 2007). In addition to well-calibrated SeaWiFS data, the key to the successful retrievals are a) the availability of high quality field data used to construct a reliable bio-optical model, and b) an aerosol model with an adjustable bimodal fraction of large versus small particles.

The approach that we will follow in this project is multifaceted:

Upgrade of NYHOPS/CDOM module in terms of CDOM photolysis kinetics

We propose to update the NYHOPS CDOM RCA code (Blumberg 2007) to include an alternative and complementary description of CDOM photodegradation to the one present currently in the model. In particular, we will include and modify as necessary the CDOM photolysis-related loss terms from the ECOSIM 2.0 formulation (Bissett 2005 and ECOSIM 2.0 manual pages 12-14 http://www.flenvironmental.org/Pubs_ppts/FERI_2004_0002_U_D.pdf). The new formulation will be complementary to the current one, so that the skill of each may be assessed.

Analyses of in situ CDOM surveys in the NY Harbor proper

We will acquire and analyze the CDOM observations made by the University of Massachussets, Boston team led by Dr. Chen inside NY/NJ Harbor waters in 2005, 2006, and 2007. Additionally, the LaTTE program has 2 weeks of cruise time in the lower estuary and plume in April of 2006. We will extract information on the shape of the CDOM absorption spectra based on AC-9 observations (absorption/attenuation intensities at 9 wavelengths), and will quantify correlations with CDOM fluorescence. Possible correlations with Chlorophyll will also be investigated. We will then use this data to: a) derive photolysis-related coefficients needed in the new alternative CDOM loss equations, b) derive coefficients needed for the new bio-optical SeaWiFS algorithm, and c) compare to the new NYHOPS/CDOM model results mentioned below.

Continued Validation of the high-resolution NYHOPS and backwards extension to calendar year 2006

Since CDOM distributions are directly related to the physical circulation, a validation of the physical circulation model is a must. A skill assessment of the high-resolution NYHOPS model for calendar year 2007 has shown that this new version (operational since January 17th 2007) improves the source tracking and hydrodynamic circulation nowcasts/forecasts compared to the older low-resolution NYHOPS version (operational since January 2004). Moreover, the high-resolution NYHOPS CDOM module has been operational only since March 30th 2007. As part of this work, we will setup and run the new high-resolution NYHOPS/CDOM model from January 1st 2006 onward, to allow for two years of high-resolution hydrodynamic circulation and CDOM fluorescence predictions. We will then assess the model skill for water level, current velocity, temperature, and salinity.

Identification of significant freshwater events for CDOM distributions analyses

With the two calendar years of CDOM model results at hand, we will identify significant freshwater events to focus on, in terms of their influence to CDOM distributions in the Harbor and, especially, the

Bight Apex. Two events that are certainly significant in the 2006-2007 time span are the near-500-year flood in upstate New York in July 2006, and the significant New Jersey tax day flooding event of 2007 (seen in Fig. 4). Significant non-freshwater events, for example Tropical Storm Ernesto and Hurricane Florence (August-September 2006) may be looked at too, depending on time availability.

Collection, storage, and analysis of SeaWiFS data for the identified events

We will collect and store SeaWiFS radiative spectral images for both the events mentioned above as well as the *in situ* sampling periods. We will process the images for clouds, and use CAO-LDISORT as well as standard SeaDAS algorithms to estimate CDOM absorption, chlorophyll concentrations, and backscatter.

Event interpretation and data-model correlations

In this final task, we will look at correlations of SeaWiFS-inferred absorbance and NYHOPS-predicted fluorescence to interpret CDOM distributions in the New York Harbor and Apex, and assess the significance of NY-Harbor-originating CDOM to CDOM concentrations in the Apex.

WORK COMPLETED

Funding for this project was not received until June 2008. We recently acquired the computer that will be used for this work, and we are in the process of installing the necessary software. We also acquired the CDOM surveys for the NY Harbor proper from Bernie Gardner of the University of Massachusetts, Boston. We started collecting SeaWiFS imagery and processing it with the CAO-LDISORT algorithm. We have started collecting the hydrodynamic data required to set up the new high-resolution NYHOPS/CDOM model from January 1st 2006 onward, to allow for two years of high-resolution hydrodynamic circulation and CDOM fluorescence predictions. In the meantime, we worked in adopting and expanding the NOAA/NOS hydrodynamic skill assessment software. Based on that, a rigorous hydrodynamic skill assessment for a period from March 1 2007 to June 10 2007, which includes the New Jersey tax day flooding event, is almost completed. Also, a new atmosphere-ocean interaction module has been developed for NYHOPS. This new surface boundary condition module provides significantly better water temperature predictions than the original model, and improves the circulation hindcast and forecast.

RESULTS

Figure 6 presents preliminary results for CAO-LDISORT-based retrievals of marine parameter distributions in the New York Bight Apex from a SeaWiFS image taken on Mar 20, 2007 at 17:47 GMT (13:47 local EDT time), along with concurrent NYHOPS CDOM forecasting results. The bottom left panel appears to depict two distinct CDOM-induced high-light-absorption areas present at that time: (1), perhaps associated with the New York Harbor plume predicted by the CDOM source tracking NYHOPS model (bottom right panel), and (2), perhaps primarily associated with a phytoplankton bloom seen in the chlorophyll retrieval. In the open ocean water, CDOM is mainly of phytoplankton origin (e.g. D' Alimonte et al 2004). Based on these results, we are considering including phytoplankton dynamics in the CDOM water quality module, so that comparisons can be drawn between the different pools.

IMPACT/APPLICATIONS

The analysis of the complementary viewpoints gained from the updated NYHOPS/CDOM source tracking model, the *in situ* observations, and the locally-calibrated remote sensing retrievals of inherent optical properties in the NY/NJ Harbor and vicinity will improve our understanding of the physicochemical processes controlling water clarity in estuarine and coastal waters. With this enhanced interpretation of CDOM sources' fate and transport, an important step toward a more complete understanding and forecasting of the dynamics controlling the apparent optical properties of water in the coastal ocean will have been achieved.

RELATED PROJECTS

- 1. Forecasting in Poorly-Sampled Estuarine Environments with Bottom Topography Mapping, Defense Advanced Research Projects Agency (DARPA), 2/1/2007 1/31/10, \$3,050,000.
- 2. The New York Bight Shelf Harbor Dynamics Study, Office of Naval Research, 04/20/06 09/30/08, \$450,000.
- 3. Phased Deployment and Operation of the Mid-Atlantic Regional Coastal Ocean Observing System (MARCOOS), NOAA Coastal Services Center, 10/1/07 9/30/08, \$643,264.
- 4. Middle East Regional Cooperation Program (MERC) Integration of Gilthead Seabream, Sparus aurata, Culture with Shellfish and Seaweeds in a Polyculture System to Increase Profitability and Reduce Environmental Enrichment, U.S. Agency For International Development, 6/1/07 5/31/10, \$247,500.
- 5. Towards a Community Sediment Transport Model, NOPP, 1/17/06 1/16/09, \$60,000.
- 6. Automated Assimilation and Fusion of Huge Volumes of Disparate Data Sets-Phase II, US Navy SBIR, 10/31/07 10/30/10, \$62,838.

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"A comparison of robust metamodels for the uncertainty quantification (UQ) of New York Harbor oceanographic data", M. C. Kerman, W. Jiang, A. F. Blumberg, and S. E. Buttrey. <u>Journal of Operational Oceanography</u>, August, 2008.

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"Quantifying Uncertainty in Estuarine and Coastal Ocean Circulation Modeling", A. F. Blumberg and N. Georgas. J. Hydraulic Engineering, 134, 403-415, 2008.

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HONORS/AWARDS/PRIZES

Alan F. Blumberg, Stevens Institute of Technology, Elected Fellow, American Society of Civil Engineering.

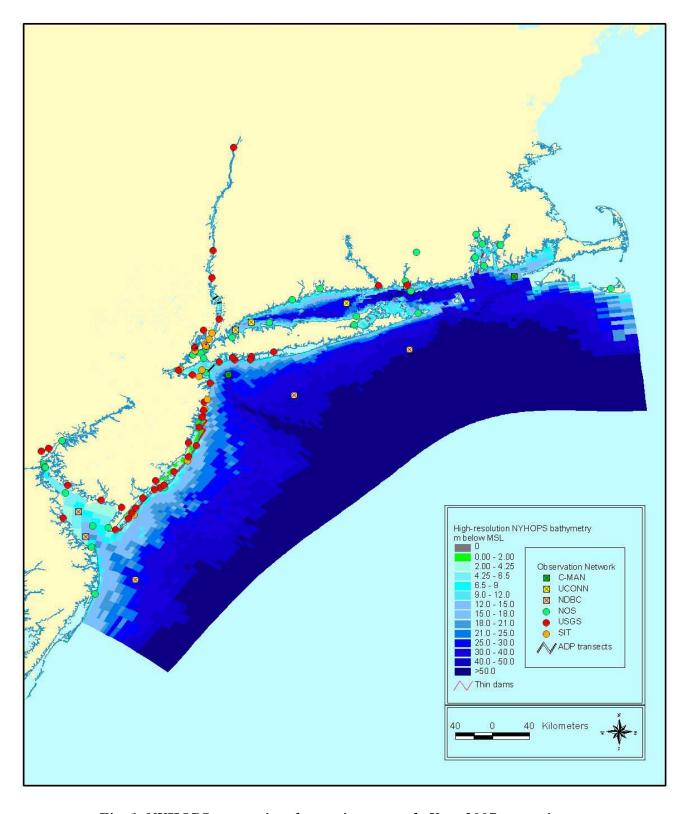


Fig. 1. NYHOPS-supportive observation network. Year 2007 expansion to include data collected by agencies other than Stevens Institute of Technology. Station locations are superimposed on the updated (since Jan 17th 2007) high-resolution NYHOPS model that includes CDOM sources and kinetics.

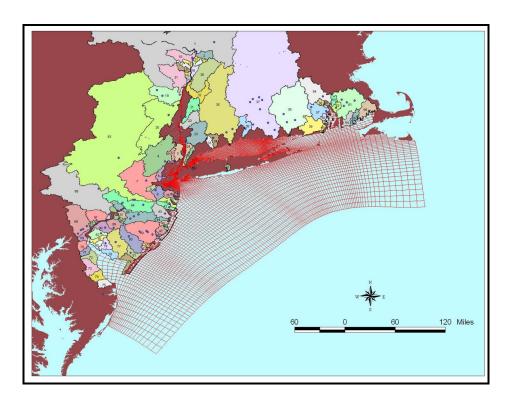


Fig. 2. Individual rivers and streams in NYHOPS (colored watershed polygons), with locations of applicable real time gages (blue dots). The variable, curvilinear, high-resolution NYHOPS grid cells are also delineated with red.

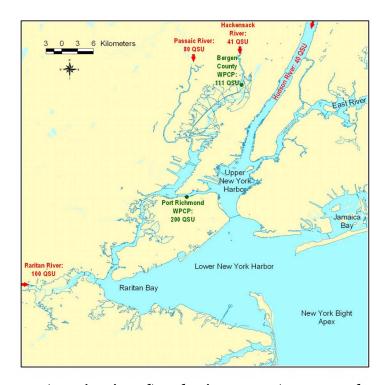


Fig. 3. Non-point source (reverine, in red) and point-source (treatment plants, in green) CDOM end-point strengths, in quantinine salinity units (QSU), as simulated in the Stevens IT NYHOPS model, based on observation-derived guidance by the Umass Boston team.

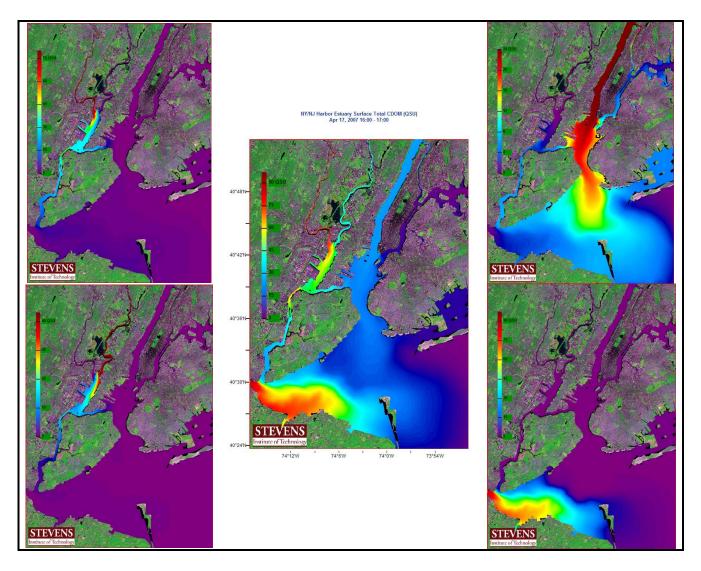


Fig. 4. Screen captures of high resolution NYHOPS-predicted CDOM for April 17, 2007 16:30 ET. This date was one of major flooding all along northern New Jersey due to very intense and longlasting rainfall. The various end members (clockwise from top left, Passaic River, Hudson River, Raritan River, and Hackensack River including the Bergen County water treatment plant), combine their strengths to create the central image which depicts the predicted CDOM fluorescence in the surface waters of the NY/NJ Harbor Estuary. Due to record-breaking river flows, fluorescence maxima in the receiving waters equaled the end member strengths of Fig. 3. Note the different scales in the end member color maps. The Hackensack river watershed inflow for this day was comparable to the inflow of the Passaic River, or two orders of magnitude higher than its historic median, making the CDOM contribution of the Bergen County plant comparatively insignificant. The contribution of the fifth end member, the Port Richmond WPCP outfall (not shown), is predicted by the model to be much less important due to an apparent 1:100 dilution factor in the vicinity of the outfall hypothesized to be due to the strong exchange of Raritan Bay, Newark Bay, and Upper Harbor waters happening through the Kills. Also visible are the mixing zone of the Hackensack and Passaic rivers (a line beginning at their confluence at Kearny Point and running along Newark Bay) and the mixing zone of the Hudson and Raritan rivers, running from Sandy Hook, NJ to Great Kills Harbor at Staten Island, NY, nicely delineating the boundaries of Raritan Bay and the Lower New York Harbor.

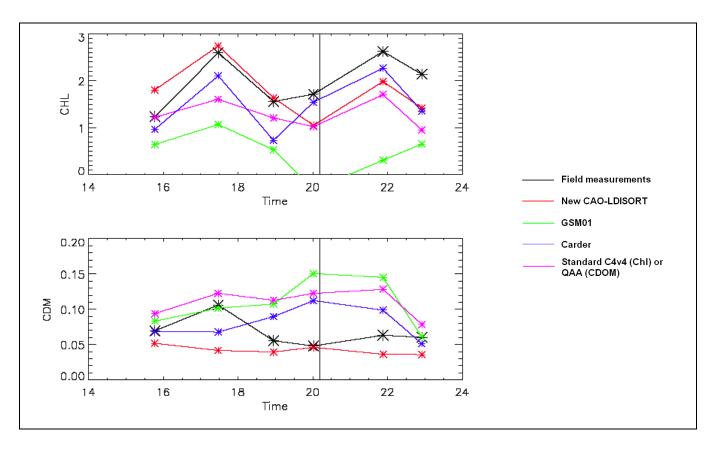


Fig. 5. In a recent paper accepted by the International Journal of Remote Sensing, Li et al compared SeaWiFS-retrieved chlorophyll concentrations (ug/L) and CDOM absorption at 443 nm (/m) from a new CAO-LDISORT algorithm they developed, against field measurements from the Santa Barbara Channel, CA taken in February 2003 and against the standard retrieval algorithms included in SeaDAS. Results showed a good correlation of the new algorithm to observations for Chlorophyll, and a smaller error for both Chlorophyll and CDOM compared to other algorithms.

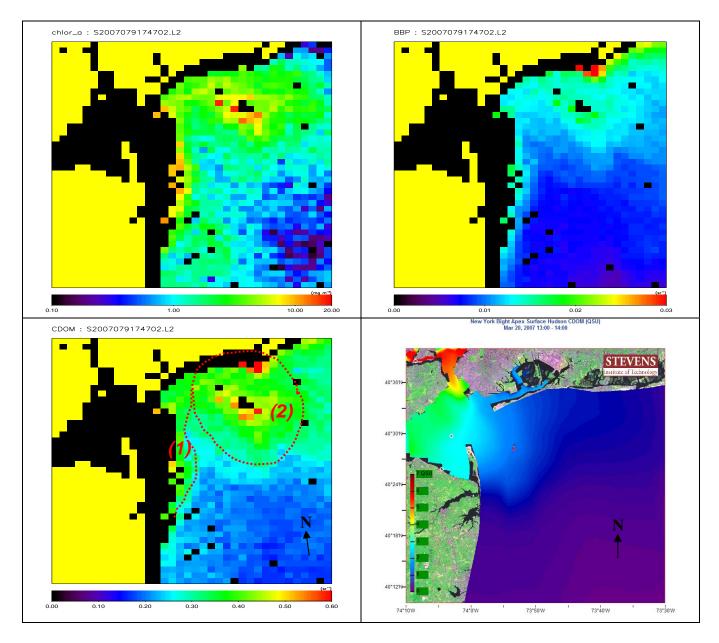


Fig. 6. Preliminary example for CAO-LDISORT-based retrievals of marine parameter distributions in the New York Bight Apex from a SeaWiFS image taken on Mar 20, 2007 at 17:47 GMT (13:47 local EDT time), along with concurrent NYHOPS CDOM forecasting results. First 3 panels show the SeaWiFS retrieved chlorophyll concentration (top left, ug/L), backscattering coefficient at 443 nm (top right, /m), and CDOM absorption coefficient at 443 nm (bottom left, /m). On these SeaWiFS retrievals, yellow areas indicate land; Black pixels are cloud/stray light pixels (no retrieval) pixels. The bottom right panel is the concurrent CDOM fluorescence (QSU) prediction from the low-resolution NYHOPS model. The bottom left panel appears to depict two distinct CDOM-induced high-light-absorption areas present at that time: (1), perhaps associated with the New York Harbor plume predicted by the CDOM source tracking NYHOPS model (bottom right panel), and (2), perhaps primarily associated with a phytoplankton bloom seen in the chlorophyll retrieval. In the open ocean water, CDOM is mainly of phytoplankton origin (e.g. D' Alimonte et al 2004).